Some Notes on Excited Electronic States

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1 Definitions

The following are a few notes from my reading of *Higher Excited States of Polyatomic Molecules*, vol. 1, by M. .B. Robin [1].

Energy regions can be associated with certain types of transitions. Robin divides the spectrum as follows:

0 - 10 000 cm^{-1}: Mostly vibrational and rotational transitions of polyatomic molecules.

10 000 - 50 000 cm^{-1}: Electronic transitions in molecules which are or unsaturated or contain lone-pairs. The presence of air presents no experimental difficulties and quartz optics may be used. The electronic transitions in this region (visible and quartz ultraviolet) can be described as valence shell transitions and hence easier for theory. In the absence of theoretical predictions, comparison to similar systems is often helpful.

50 000 - 100 000 cm^{-1}: This is the vacuum ultraviolet, a much more treacherous region. Quartz is opaque in this region and must be replaced by high-quality sapphire or salt optics or other spectroscopic techniques must be used. The solvents and the presence of air may also hamper experiments. Furthermore, the density of valence transitions with repsect to wavenumber increases dramatically after 50 000 cm^{-1} (it tails off again eventually, at a few hundred thousand wavenumbers), making theoretical modelling and assignment difficult. Even worse, Rydberg transitions typically begin around 50 000 cm^{-1}. This energy region is the focus of Robin's work.

100 000 + cm^{-1}: The extreme vacuum-ultraviolet region; there are no longer transparent, strong window materials, and transitions are often ionizing or autoionizing.

A few other definitions regarding the transitions are in order:

Vertical: The most intense band in the vibrational Franck-Condon envelope.

Adiabatic: The frequency for a transition where both upper and lower states have no vibrational quanta (i.e., a transition between zero-point levels).

Advertical: A transition which is both vertical and adiabatic.

2 Rydberg Transitions

Sharp transitions often occur in a series described by the hydrogen-like formula

$$h\nu = \epsilon_i - \frac{R}{(n-\delta)^2}, \tag{1}$$

where ϵ_i is the ionization potential to which the series converges, R is the Rydberg constant, n is the quantum number (which reaches infinity at ϵ_i), and δ is called the quantum defect. Such transitions are described as “Rydberg transitions.” However, it is also possible that Rydberg transitions may not be sharp and therefore not easily fit to the above equation. Broad transitions might also be valence transitions, and Robin notes that researchers at one time had a propensity to assume that any broad transition was a valence transition. In the vacuum-ultraviolet, valence and Rydberg states are much more likely to mix than they are in the quartz-ultraviolet.

Rydberg states can be defined as those which fit Eq. (1) and whose wavefunctions are appropriate to generate such a series. Excitation energies are often reported as the difference between the Rydberg state and the corresponding ionization limit; these are referred to as “term values” in this context. For theoretical work, it may be more desirable to compute these term values than the actual excitation energies because the Rydberg state should look more like the ion than the ground state; orbital relaxation and correlation effects are more likely to cancel.

While any particular valence transition may also fit Eq. (1), it will not belong to a series with increasing quantum number n. An electron in a polyatomic molecule will fit such a formula if it is very diffuse, so that the core appears as a point charge. Of course this will never be entirely true, so the parameter δ is added to correct for the extent to which the distant electron penetrates the core. The ground state of an atom may have an electron with a large radius and may thus be referred to as a Rydberg state; for neutral polyatomics, this never happens. Rydberg transitions may be split by core asymmetries, but the splittings decrease with increasing n because the core becomes better modeled as a point charge as the electron radius increases.

For second-row atoms and molecules, the general trends in δ are:

ns: Penetrate the core to a large extent; $\delta \approx 1$.

np: Penetrate to a moderate extent; $\delta \approx 0.6$.

nd: Hardly penetrate the core; $\delta \approx 0$.

For lower rows of the periodic table, more general rules are required. A Rydberg orbital will be nonpenetrating ($\delta \approx 0$) if the core does not contain any occupied orbitals of its symmetry. Mulliken refers to such core orbitals as "real precursors." Hence $\delta \approx 0$ for, e.g., 2p, 3d, and 4f Rydberg orbitals of lithium, sodium, and potassium, respectively. Unoccupied orbitals of the same symmetry and below the Rydberg orbital are called "virtual precursors," although I don't know what effect such orbitals have on δ. The effect of real precursors on δ can be understood because of the Rydberg AOs must be orthogonal to the occupied AOs. For orbitals of the same symmetry type, the orthogonality must be brought about in the radial wavefunction. If the core AO has n loops ($n-1$ radial nodes) and the Rydberg orbital has $n+1$ loops (n radial nodes), then the Rydberg orbital can be (must be?) made by adding a loop which is out of phase with the tail of the occupied orbital. Since the overall overlap must be zero, the radial wavefunctions will be in-phase near the core region and hence have similar penetrating properties (and thus similar δ values). Robin claims that the penetrating properties of a Rydberg orbital decrease as n increases since the orbital must be normalized (fair enough), and that this is already reflected in that as n increases, $(n-\delta)$ approaches n^2. This last point seems odd; I should think that arguments about extent of penetration would affect δ itself (of course this would lead to n-dependent δ's and would complicate the formula). Conversely, if there are no real precursors, the Rydberg orbital can achieve orthogonality to core orbitals through its angular part and is free to be (but must it be?) nonpenetrating. In a somewhat more mathematical treatment, Robin summarizes arguments by Mulliken that the lowest Rydberg orbital looks the same as its real precursor, to which an additional hydrogenic loop has been added with a phase shift intimately related to δ; this is called "recapitulation."

The preceeding analysis is of course not directly applicable to polyatmoic molecules. Indeed, a nonpenetrating AO on one center may still penetrate another center, suggesting that Rydberg orbitals in polyatomics are generally more penetrating. The recapitulation idea is now not nearly as simple, since the Rydberg orbital must be orthogonalized against other occupied orbitals which may have no overlap with the precursor. Generally $\delta(n\mathrm{s}) > \delta(n\mathrm{p}) > \delta(n\mathrm{d})$ still holds, but now quantum mechanical exchange has an effect.

So far, the discussion of penetration has implicitly assumed an effect of the form

$$E_{\text{pen}} = -\langle \phi_R | \frac{Z-1}{r} | \phi_R \rangle + \sum_{\text{core}} (\phi_R \phi_R | \phi_C \phi_C). \tag{2}$$

This expression makes it clear that the exchange effect has been neglected

$$E_{\text{ex}} = -\sum_{\text{core}} (\phi_R \phi_C | \phi_R \phi_C) \pm (\phi_R \phi'_C | \phi_R \phi'_C) \tag{3}$$

where the sums are only over doubly occupied core orbitals and C' represents a half-filled core orbital if appropriate (contributing to a two-electron integral entering with a + or - sign for singlets or triplets, respectively). As for E_{pen}, E_{ex} is expected to decrease with increasing n and to be small when the core has no real precursors. Exchange is twice as large as penetration for Li, but becomes less important for Li and Be (it has a positive sign for the singlet states). It is presumed that the exchange term becomes small compared to penetration for larger atoms.

For polyatomics, the Rydberg states can mix heavily. For NO, 3s is unperturbed by mixing, but above that ns mixes strongly with $(n-1)$dσ, making the ndσ series have a negative δ. Actually this makes sense in that δ for nd is about 0 whereas δ for ns is about 1.0, so ns and $(n-1)$d orbitals are about degenerate. The ns orbitals are a bit lower, so mixing causes the $(n-1)$d orbitals to be slightly raised in energy and hence they acquire a negative δ (their binding energy becomes slightly smaller than in hydrogen).

The singlet-triplet splitting of a pair of Rydberg states should be small because, at the SCF level, this splitting is roughly $2K$, and for Rydberg states the exchange integral should be relatively small. In most polyatomic molecules, the singlet-triplet splitting of Rydberg states is typically less than 5000 cm^{-1}. One exception to this rule is found found for ethylene, where the $(\pi, 3\text{d}\pi)$ singlet Rydberg configuration is strongly mixed with the singlet valence configuration (π, π^*). However, the correspoding triplet configurations are not mixed, and thus the singlet-triplet splitting is not given by something like $2K$.

For polyatomics there is an additional difficulty in determining whether an orbital is Rydberg or unoccupied valence; for example, in methane the carbon 3s orbital has the same nodal structure as the antibonding σ orbital. Such orbitals are called a conjugate pair. Mulliken claims that these are alternative descriptions of the same orbital; however, Robin argues that in the above example the 3s orbital is nonbonding while σ^* is antibonding and that numerous calculations support the idea of separate valence and Rydberg states. In ethylene, the valence shell (π, π^*). and Rydberg $(\pi, 3\text{d}\pi)$ configurations have the same nodal patterns, and the V state has been attributed to each of these separately. Now the prevailing view is that the state does not fit the Rydberg formula and is primarily a valence transition with some Rydberg character mixed in. In the triplet manifold, the analogous configurations give rise to distinct valence and Rydberg states. If mixing of the conjugate pair is large, then it can in fact add a node to the Rydberg orbital, which makes it possible to describe the orbital as $n+1$ instead of n (and this is the practice of some authors). However, the size of the orbital and the frequency from Eq. (1) is much closer to that expected for n.

Oscillator strengths of Rydberg transitions are governed by the transition moment matrix element

$$\mu = \langle \phi_C | \mathbf{r} | \phi_R \rangle. \tag{4}$$

As n increases, $\phi_C \phi_R$ decreases and the oscillator strength has an n^{-3} dependence. Also, atomic selection rules on this matrix element ($\Delta l = \pm 1$) can remain important at least for diatomics. The oscillator strength of the lowest Rydberg transition in a series never exceeds 0.08 per degree of degeneracy, whereas for valence shell transitions values of 0.3-1.0 are easy to achieve (the V state transition in ethylene has 0.34).

Robin notes that Rydberg orbitals are important even for valence transitions. He argues—somewhat hand-wavingly—that altough triplet valence states are partially correlated at the Hartree-Fock level leading to adjustments in the orbitals involved in the excitation, singlet states must be correlated by configuration interaction and that such correlation desires to mix in orbitals of Rydberg character. He cites the example of ethyelene, where calculations at the SCF and CI levels both give too-high excitation energies; when Rydberg orbitals are added, the SCF and CI results match experiment much more closely.

The following generalizations are given for Rydberg transitions converging on ionization potentials other than the first:

- Rydberg excitations beyond the first ionization potential are typically broadened by autoionization and appear as a broad band on the continuum.
- Since Rydberg oscillator strengths fall off rapidly in a series (theoretically as n^{-3}), only the first one or two transitions in a series may be observed.
- The Rydberg term values (see above for special definition of term value) are largely independent of originating MO. Hence term values for the first ionization potential can be used to predict or identify Rydberg excitations beyond the first ionization potential.

Experimentally, one way to distinguish between valence and Rydberg excitations is that the Rydberg excitations can be sensitive to a "perturber gas." This is rationalized by the diffuse nature of the excited electron. Dramatic effects can be produced by perturber gasses with partial pressures of only ~ 100 atm. Of great value is the fact that the perturber gas causes pressure broadening of the absorber only to higher frequencies. In contrast, using higher concentrations of the absorber gas (the perturber is the absorber) causes pressure broadening to higher and lower frequencies of both Rydberg and valence excitations. In cases where the excitations appear as continuous bands, the pressure effect is useless unless it is greatly magnified; this can be accomplished by trapping the absorber in a low-temperature rare-gas matrix, by dissolving it in a transmitting solvent, or by forming a polycrystalline film of the neat absorber at low temperatures. The lowest Rydberg excitation energy of a dilute guest molecule in a rare-gas host will increase by 2000-5000 cm^{-1} compared to the gas-phase spectrum, and the vibronic bandwidths will be 200-500 cm^{-1}. By contrast, most valence shell excitations will experience a redshift of 1000-3000 cm^{-1}. If placed in a low-mobility organic matrix, valence excitations behave similarly but Rydberg excitations can broaden sufficiently as to disappear. The V state of ethylene behaves as a valence excitation under perturbations. For diatomics and presumably for polyatomics, in condensed phases coupled Rydberg and valence states can become uncoupled.

References

[1] M. B. Robin, *Higher Excited States of Polyatomic Molecules*, volume 1. Academic Press, New York, 1974.